# Photochemical Formation of 1,5-Diketones from Dibenzoylmethane and Some Quinones

**Sung Sik Kim,\* Jin Sun Lim, Jong Myung Lee, and Sang Chul Shim[†]**

*Department of Chemistry, Chonbuk National University, Chonju 561-756, Korea*
*[†]Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea*
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Irradiation (300 nm UV light) of dibenzoylmethane and 1,4-naphthoquinone in dichloromethane gave 1,5-diketone as the major product, along with $\beta$-hydroxyketone as the minor product. Anthraquinone and anthrone also added photochemically to dibenzoylmethane to give 1,5-diketones as the major products. In contrast, tetrahalo-1,4-benzoquinones added to dibenzoylmethane to give two types of 1,5-diketones *via* oxetane and cyclobutane intermediates. Comparison of the potential energy values of the photoproducts reveals that the 1,5-diketones are more stable than the corresponding oxetanes or cyclobutanes due to the ring-strain of the bicyclic compounds.

## Introduction

Quinones are an important class of compounds as quinone dye-stuffs in industry or dehydrating agents in organic synthesis in addition to a vital role in biological systems. Due to their various spectroscopic properties, the photochemistry of quinones has been a subject of extensive investigations in many areas.[1-4] The synthetic significance of the intermolecular enone-alkene photocycloaddition was extended by irradiating $\beta$-diketones in the presence of alkenes to produce 1,5-diketones.[5] The enolic form of the $\beta$-diketone, which is restricted in six-membered ring by an intramolecular hydrogen bond, is an intermediate. Our interest in the diverse reactivity of excited quinones has promoted us to investigate the type of the photoproducts of some *p*-quinones and $\beta$-diketones. Recently, we reported, for the first time, that dibenzoylmethane **1** adds to *p*-benzoquinone **2** to give 1,5-diketone **4**, as shown in Scheme 1.[6] We report here that irradiation of some quinones and a $\beta$-diketone, *i.e.*, dibenzoylmethane **1**, gives 1,5-diketones *via* initially formed $\beta$-hydroxy ketone **3** as oxetane intermediate. In the case of tetrahalo-1,4-benzoquinones, the photoproducts were found to be two types of 1,5-diketones by way of the corresponding $\beta$-hydroxyketones.

## Experimental Section

**Materials.** *p*-Benzoquinone, tetrachloro-1,4-benzoquinone, tetrabromo-1,4-benzoquinone, 1,4-naphthoquinone, anthraquinone, and dibenzoylmethane were purchased from Aldrich Chemical Co. and used as received or recrystallized prior to use. Dichloromethane, *n*-hexane, and ethyl acetate were distilled prior to use. Silica gel (Kieselgel 60, 230-400 mesh, Merck Co.) was used for column chromatography. Analytical thin layer chromatography (TLC) plates were purchased from Merck Co. as aluminum sheets (20×20 cm) precoated with 0.25 mm silica gel together with fluorescent indicator.

**Instruments.** 400 MHz $^1$H spectra were recorded on a
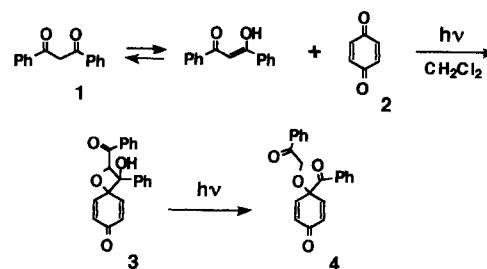


**Scheme 1**

Jeol JMN EX NMR spectrometer. Chemical shifts, $\delta$, were reported as parts per million (ppm) downfield from internal tetramethylsilane (TMS) standard. Infrared (IR) spectra were recorded on a Nicolet 5-DX 13 Fourier Transform spectrophotometer in KBr pellets or NaCl cells. Ultraviolet (UV) spectra were obtained on Beckman DU 7500 spectrophotometer. Mass spectra were determined on a Hewlett Packard 5985 GC/MS system using electron impact method.

**General procedure for the photocycloadditions of dibenzoylmethane to quinones.** Preparative photoreactions were conducted in a photoreactor composed of a water-cooled inner condenser and a Pyrex reaction vessel with 300 nm UV lamps (Rayonet Photochemical Reactor, Model RPR-208), after purging with nitrogen gas (purity; 99.9%) for 30 min. The reaction mixture was concentrated in vacuo and chromatographed over silica gel with *n*-hexane and ethyl acetate as the eluent.

When a dichloromethane solution (100 mL) of dibenzoylmethane **1** (135 mg, 0.6 mmol) and 1,4-naphthoquinone **5** (95 mg, 0.6 mmol) was irradiated with 300 nm UV light for 110 h, the consumption of starting material was associated with the formation of two photoproducts. Separation and isolation of both products were accomplished by flash column chromatography (silica gel, 230-400 mesh) using *n*-hexane and ethyl acetate (10 : 1, v/v) as the eluents to give a $\beta$-hydroxyketone **6** (15%) as spiro-oxetane and 1,5-diketone **7** (27%). **6**: UV (MeOH) $\lambda_{max}$ 330, 248 nm; IR (KBr) 3335, 3066, 2952, 1716, 1669, 1441, 1270, 1072 cm$^{-1}$; 400 MHz

$^1$H NMR (CDCl$_3$) $\delta$ 16.2 (1H, s, OH), 8.2-7.3 (14H, m, Ar), 6.63 (1H, s, CH), 6.57 (1H, d, $J$ = 7.9 Hz, =CH), 6.47 ppm (1H, d, $J$ = 7.9 Hz, =CH); Mass (EI) m/e 382 (M), 105, 77. **7**: UV (MeOH) $\lambda_{max}$ 325, 243 nm; IR (KBr) 3073, 2952, 1743, 1696, 1596, 1461, 1246, 1091 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 8.3-7.3 (14H, m, Ar), 6.65 (2H, s, CH$_2$), 6.57 (1H, d, $J$ = 7.9 Hz, =CH), 6.54 (1H, d, $J$ = 7.9 Hz, =CH); Mass (EI) m/e 382 (M), 105, 77.

Irradiation of a dichloromethane solution (200 mL) of dibenzoylmethane **1** (224 mg, 1.0 mmol) and anthraquinone **11** (208 mg, 1.0 mmol) with 300 nm UV light for 60 h afforded $\beta$-hydroxy ketone **12** and 1,5-diketone **13** in 11% and 32% yields, respectively. **12**: UV (MeOH) $\lambda_{max}$ 350, 272, 253 nm; IR (KBr) 3402, 2983, 1723, 1682, 1454, 1239, 1085, 1024 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 9.97 (1H, s, OH), 8.30-7.30 (18H, m, aromatic), 6.86 (1H, s, CH); Mass (EI), m/e 432 (M). **13**: UV (MeOH) $\lambda_{max}$ 273, 240 nm; IR (KBr) 1723, 1696, 1447, 1125, 1017 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 8.2-7.2 (18H, m, aromatic), 5.60 (2H, s, CH$_2$); Mass (EI), m/e 432 (M).

Irradiation of a dichloromethane solution (100 mL) of dibenzoylmethane **1** (224 mg, 1.0 mmol) and anthrone **14** (194 mg, 1.0 mmol) with 300 nm UV light for 110 h afforded $\beta$-hydroxy ketone **15** and 1,5-diketone **16** in 18% and 29% yields, respectively. **15**: UV (MeOH) $\lambda_{max}$ 340, 253 nm; IR (KBr) 3375, 3079, 1716, 1340, 1044 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 11.92 (1H, s, OH), 8.3-7.3 (16H, m, Ar), 6.86 (1H, s, CH), 5.55 (2H, s, CH2); Mass (EI), m/e 418 (M), 105, 77. **16**: UV (MeOH) $\lambda_{max}$ 340, 273, 253 nm; IR (KBr) 2985, 1669, 1548, 1125, 1044 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 8.36-7.30 (16H, m, aromatic), 6.86 (2H, s, CH$_2$), 4.35 (2H, s, CH2); Mass (EI), m/e 418 (M), 105, 77.

Irradiation of a dichloromethane solution (100 mL) of dibenzoylmethane **1** (179 mg, 0.8 mmol) and tetrachloro-1,4-benzoquinone **17a** (197 mg, 0.8 mmol) with 300 nm UV light for 120 h afforded 1,5-diketones **19a** (X=Cl) and **21a** (X=Cl) in 24% and 13% yields, respectively. **19a**: UV (MeOH) $\lambda_{max}$ 338, 290, 248 nm; IR (KBr) 2952, 1729, 1682, 1273, 1071, 755 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 8.0-7.3 (10H, aromatic), 4.69 (2H, s, CH$_2$); Mass (EI), m/e 470 (M), 105, 77. **21a**: UV(MeOH) $\lambda_{max}$ 330, 284, 247 nm; IR (KBr) 2948, 1715, 1689, 1287, 1192, 725 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 7.95-7.30 (10H, aromatic), 7.03 (2H, s, CH$_2$); Mass (EI), m/e 470 (M), 105, 77.

Irradiation of a dichloromethane solution (100 mL) of dibenzoylmethane **1** (179 mg, 0.8 mmol) and tetrabromo-1,4-benzoquinone **17b** (339 mg, 0.8 mmol) with 300 nm UV light for 120h afforded 1,5-diketones **19b** (X=Br) and **21b** (X=Br) in 10% and 7% yields, respectively. **19b**: UV (MeOH) $\lambda_{max}$ 341, 296, 258, 238 nm; IR (KBr) 2918, 1776, 1689, 1266, 929 cm$^{-1}$; 400 MHz $^1$H NMR(CDCl$_3$), $\delta$ 8.0-7.3 (10H, aromatic), 6.84 (2H, s, CH$_2$); Mass (EI), m/e 648 (M), 105, 77. **21b**: UV(MeOH) $\lambda_{max}$ 336, 287, 250 nm; IR (KBr) 2958, 1709, 1588, 1273, 1199, 742 cm$^{-1}$; 400 MHz $^1$H NMR (CDCl$_3$), $\delta$ 7.3-8.0 (10H, aromatic), 4.47 (2H, s, CH$_2$); Mass (EI), m/e 648 (M), 105, 77.

## Results and Discussion

The synthetic significance of the intermolacular enone-alkene photocycloaddition was found to be extended by irradiating 1,3-diketone, *i.e.*, dibenzoylmethane **1** and some quinones in dichloromethane to produce 1,5-diketones. Recently, we found, for the first time, that the enol form of dibenzoylmethane **1** added to *p*-benzoquinone **2** to give aldol, *i.e.*, $\beta$-hydroxyketone **3** and 1,5-diketone **4**.[6] The final product **4** is thought to be formed by a retro-aldol type ring opening of the $\beta$-hydroxyketone **3**. We describe here that irradiation of dibenzoylmethane and some quinones with 300 nm UV light leads to 1,5-diketones *via* initially formed spiro-oxetanes. 1,4-Naphthoquinone is known to undergo the photoaddition reaction to olefins or alkynes at C=O or C=C bond of the structure. The photoaddition reaction of dibenzoylmethane **1** to 1,4-naphthoquinone **5** gave spiro-oxetane **6** and 1,5-diketones **7**, as shown in Scheme 2.

The preferential formation of aldol **6** to alternative isomer may be rationalized by comparing the two 1,4-diradical intermediates, **8** and **9**, as shown in Figure 1.[6,7] Consistent with the experimental results, the 1,4-diradical intermediate **8** having ketyl-like tertiary radical is more stable than **9** having secondary radical. Thus, the 1,5-diketone **7** may be formed *via* the more stable 1,4-diradical intermediate **8**, followed by the intramolecular cyclization reaction to give keto-oxetane **6**, and finally undergoes retro-aldol type ring opening to give the 1,5-diketone **7**.

The 1 : 1 adduct **6** was found to reverse to the starting materials **1** and **5**, when irradiated **6** with 254 nm UV light in dichloromethane. Interestingly, irradiation of **7** with 300 nm UV light in dichloromethane gave **6**, which may be interpreted by Norrish type II raction[8,9] as follows. Excited carbonyl compounds **7** having a $\gamma$ hydrogen atom undergo a characteristic 1,5-hydrogen atom transfer by an intramolecular cyclic process with the formation of a ketyl-like 1,4-diradical **10**, and finally the cyclization to give a spiro-oxetane **6**, as shown in Scheme 3.
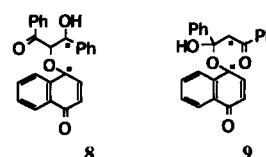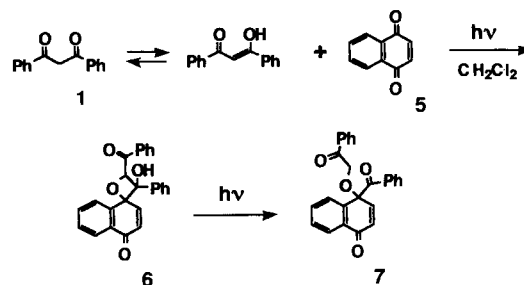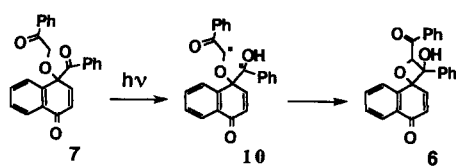
Dibenzoylmethane **1** was also found to added to

**Scheme 2**

**Figure 1**

**Scheme 3**

anthraquinone **11** to give the corresponding spiro-oxetane **12** and its retro-aldolization product, *i.e.*, 1,5-diketone **13**, in 11% and 33% yield, respectively, when irradiated dibenzoyl-methane **1** and anthraquinone **11** with 300 nm UV light in dichloromethane (see Figure 2). In the similar manner, anthrone **14** also added to dibenzoylmethane **1** to give aldol **15** and 1,5-diketone **16**, in 13% and 29% yield, respectively, when irradiated dibenzoylmethane **1** and anthrone **14** with 300 nm UV light in dichloromethane (see Figure 2). The reversible Norrish type II cyclization reaction was observed between the two isomers **12** and **13**.

In sharp contrast, tetrahalo-1,4-benzoquinones **17a** and **17b** were found to add to dibenzoylmethane **1** to yield two types of 1,5-diketones **19a** and **19b**, and **21a** and **21b** (a: X = Cl, and b: X = Br), respectively. Unlike 1,4-benzoquinone **2**, tetrahalo-1,4-benzoquinones **17a** and **17b** added to C=C bond as well as C=O bond of the *p*-quinones **17** to give aldols as spiro-oxetanes **18a** (X=Cl) and **18b** (X=Br) and as cyclobutanes **20a** (X=Cl) and **20b** (X=Br), which were also found to undergo retro-aldolization to give 1,5-diketones **19a** (and **19b**) and **21a** (and **21b**), respectively.[10] The formation of 1,5-diketones **21a** and **21b** implies that cyclobutanes **20a** and **20b** are formed *via* 1,4-diradical intermediate which may be stabilized by chlorine or bromine atom. In the case of the 1,4-diradical, the lone pair electrons of the radical cen-
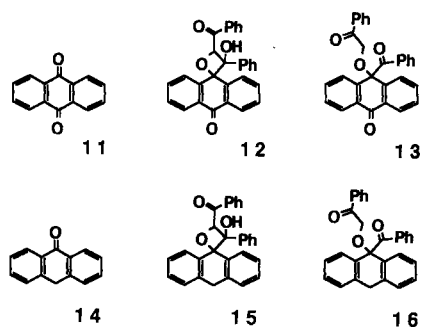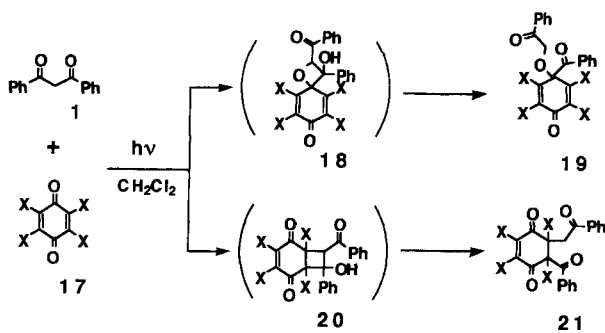


**Figure 2**



**Scheme 4**

**Table 1.** Potential energy values of the photoadducts of dibenzoyl-methane and some quinones obtained by MM2 calculation

| Potential energy of the photoproducts as oxetanes or cyclobutanes | | Potential energy of the photoproducts as 1,5-diketones | | Energy difference between oxetanes (or cyclobutanes) and 1,5-diketones (kcal/mol) |
|---|---|---|---|---|
| Com-pounds | Energy (kcal/mol) | Com-pounds | Energy (kcal/mol) | |
| 3 | 34.16 | 4 | 21.40 | $\Delta E_{3-4}$    12.76 |
| 6 | 34.41 | 7 | 22.15 | $\Delta E_{6-7}$    12.26 |
| 12 | 33.74 | 13 | 18.71 | $\Delta E_{12-13}$    15.03 |
| 18a | 56.81 | 19a | 48.33 | $\Delta E_{18a-19a}$    8.48 |
| 18b | 60.45 | 19b | 50.89 | $\Delta E_{18b-19b}$    9.56 |
| 20a | 83.08 | 21a | 69.43 | $\Delta E_{20a-21a}$    13.65 |
| 20b | 83.17 | 21b | 67.07 | $\Delta E_{20b-21b}$    16.10 |

ter can further delocalize onto the halogen, and this reso-nance stabilization allows the 1,4-diradical to be more stable.

The relative stability of the two types of photoproducts, *i.e.*, oxetanes (or cyclobutanes) and 1,5-diketones, was com-pared by calculating the potential energy values of their min-imized structures using MM2 calculation as shown in Table 1.[11] The preference of the formation of 1,5-diketones to oxe-tanes (or cyclobutanes) could be determined by calculating the energy differences between the two types of photoprod-ucts. The table reveals that the cyclic products as oxetanes or cyclobutanes are less stable than the corresponding 1,5-dike-tones, in which the latter is free from the ring strain. The potential energy differences ($\Delta E_{6-7}$ and $\Delta E_{12-13}$) between the two types of photoadducts were 12.26 and 15.03 kcal/mol. The photoproducts (**18a** to **21a**) obtained from tetrachloro-1,4-benzoquinones **17a** were found to be less stable than the adducts (**3, 4, 6, 7, 12**, and **13**) come from *p*-benzoquinone **2**, 1,4-naphthoquinone **5**, and anthraquinone **11**. This result may be due to the steric hindrance by the chlorine atoms in the structure. The preference of the formation of the 1,5-diketone **21b** to oxetane **20b** was calculated to be the great-est ($\Delta E_{20b-21b}$ = 16.10 kcal/mol). Energy difference ($\Delta E_{20a-18a}$) between oxetane **18a** and cyclobutane **20a** was calcu-lated to be 26.27 kcal/mol, which implies that the oxetane may be formed easier than the cyclobutane. As shown in Table 1, the oxetanes **18** undergo easily retro-aldolization to give the more stable 1,5-diketones **19**. In the same manner, the cyclobutanes **20** are so unstable that they undergo easily retro-aldolization to give the corresponding 1,5-diketones **21**.

In conclusion, we have found that 1,5-diketones can be produced photochemically from the enolic form of 1,3-dike-tone and some quinones. The potential energy values obtained by MM2 calculation shows that 1,5-diketones are more stable than the oxetanes or cyclobutanes. The relative stability of the photoadducts of dibenzoylmethane to *p*-ben-zoquinone, 1,4-naphthoquinone, and anthraquinone were found to be similar with each other. On the other hand, the photoproducts of dibenzoylmethane and tetrahalo-1,4-ben-zoquinones were found to be less stable than those of 1,4-

benzoquinone, 1,4-naphhoquinone, and anthraquinone. The physical and chemical properties of the photoproducts and the photoreactivity of various 1,3-diketones toward quinones and related compounds will be investigated.

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7. A cyclic aldol as spiro-oxetane was also isolated from the photoreaction of 1,3-cyclohexanedione with *p*-benzoquinone in dichloromethane as the minor product. The addition was found to occur at C=O bond of *p*-benzoquinone and C=C bond of the enolic form in 1,3-cyclohexanedione. Spectral data of the adduct: $^1$H NMR (CDCl$_3$) $\delta$ 9.58 (1H, s), 7.15 (2H, d), 6.97 (2H, d), 6.45 (1H, s), 3.02 (2H, t), 2.64 (2H, t), 2.36 (2H, m); IR (KBr) 2958, 2925, 1729, 1461, 1266, 1125, 722 cm$^{-1}$; Mass (EI) m/e 220 (M).

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10. Such two isomeric adducts, *i.e.*, oxetane and cyclobutane, were also found in the photoaddition of 1,4-naphthoquinone to 1,4-diethynylbenzene. For this reaction, see Kim, S. S.; O. K. J.: Shim, S. C. *Bull. Korean Chem. Soc.* **1994**, *15*(4), 270.

11. MM2 calculation was carried out using CambridgeSoft Chem 3D 4.0 for Windows and Macintosh program, by considering energy terms such as stretch, bend, stretch-bend, torsion, non-1,4 van der Waals, 1,4 van der Waals, and dipole/dipole.